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Synthesis and characterization of liquid crystals containing a non-activated 1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] group†

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Two series of mesogens derived from the non-activated spiropyran dyes 6-hydroxy-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (series **1**) and 6-(4-hydroxyphenyl)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (series **2**) have been synthesized. Analysis by differential scanning calorimetry, polarizing microscopy and X-ray diffraction showed that compounds in series **1** form monotropic nematic and SmA phases, while compounds in series **2** form only a monotropic nematic phase. One compound in series **1**, 1′,3′,3′-trimethylspiro-[2*H*-1-benzopyran-2,2′-indoline)-6-yl 4′-octyloxybiphenyl-4-carboxylate (**1b**), was also shown to form a monotropic SmC phase between 71 and 60°C.

1. Introduction

Photochromic indolinobenzospiropyran (spiropyran) dyes have been extensively studied due to their potential applications in many new technologies, including high-density optical data storage, optical switching, displays and non-linear optics [1, 2]. Thus far, most studies have focused on derivatives of 1′,3′,3′-trimethyl-6-nitrospiro-[2*H*-1-benzopyran-2,2′-indoline] due to its propensity to undergo photochemical ring opening to a stable merocyanine form. Much less attention has been paid to so-called non-activated spiropyrans, which lack a strong electron-withdrawing group that stabilizes the coloured merocyanine form [3–5]. Upon irradiation, these species usually give rise to a photostationary state with a negligible merocyanine concentration, which is undesirable for most photochromic applications. However, because the merocyanine form is prochiral, such a photostationary state effectively results in the photo-racemization of the chiral spiropyran group, which is an essential requirement for photoresolution [6]. We are currently investigating the chiroptical properties of several non-activated spiropyrans in order to develop a ferroelectric liquid crystal optical switch based on the principle of photoresolution. In order to maximize the switching efficiency of these materials, we sought to develop smectic C (SmC) mesogens that incorporate a non-activated spiropyran moiety.

Only a few examples of spiropyran-containing mesogens have been reported. Krongauz and co-workers reported the synthesis of (4-alkoxybenzoyloxy)benzylidene derivatives of 5′-amino-1′,3′,3′-trimethyl-6-nitrospiro-[2*H*-1-benzopyran-2,2′-indoline], which exhibited a so-called quasi-liquid crystal phase with physical characteristics analogous to that of a nematic phase [7–9]. This mesophase was observed only upon heating a metastable amorphous film of the spiropyran derivatives; the crystalline form did not exhibit a mesophase. Other reports of spiropyran-containing mesogens refer to the incorporation of 5′-amino-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] or a 3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] group tethered at the 1′-position as photochromic and/or thermochromic side-chains in polymeric nematic liquid crystals and cyclic siloxanes [10–14]. In all these cases, the incorporation of spiropyran groups was shown to

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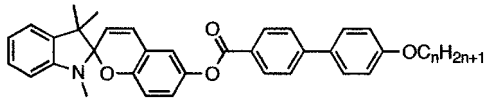
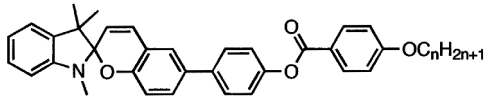
cause a significant decrease in the mesophase temperature range. In this paper, we report the synthesis and characterization of two series of non-activated spiropyran derivatives, **1** and **2**, which form monotropic liquid crystal phases. One of these compounds, **1b**, forms a monotropic SmC phase between 71 and 60°C.



1a, n = 7; **1b**, n = 8; **1c**, n = 9; **1d**, n = 10; **1e**, n = 12



2a, n = 5; **2b**, n = 7; **2c**, n = 8; **2d**, n = 9; **2e**, n = 10

2. Experimental

2.1. *General*

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained in deuteriated chloroform and deuteriated DMSO on a Bruker ACF-200, AM-400 or AMX-500 NMR spectrometer. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low-resolution EI mass spectra were obtained using a Fisons VG Quattro triple quadrupole mass spectrometer; peaks are reported as *m/z* (% intensity relative to base peak). High-resolution EI mass spectra were obtained by the University of Ottawa Regional Mass Spectrometry Centre. UV spectra were recorded on a Varian Cary 3 UV–visible spectrometer in cyclohexane. Differential scanning calorimetry analyses were carried out using a Perkin-Elmer DSC-7 instrument calibrated with indium at a heating/cooling rate of 3°C min^{-1}. Characterization of liquid crystal textures was achieved using a Nikon Labophot-2 polarizing microscope equipped with an Instec HS1-i hot stage. X-ray analyses were carried out at the Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM) of Université Laval using a Rigaku Rotaflex RU-200BH rotating anode, with Ni-filtered Cu K_α radiation, operating at 55 kV/190 mA. Wide angle and small angle profiles were recorded using Rigaku scintillation counters coupled to pulse-height analysers.

2.2. *Materials*

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Dichloromethane was distilled from P_2O_5 immediately prior to use. 6-Hydroxy-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (**5**) and 6-(4-hydroxyphenyl)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (**7**) were prepared by condensation of 2-methylene-1,3,3-trimethylindoline (**3**) with 5-hydroxysalicylaldehyde (**4**) and 5-(4-hydroxyphenyl)salicylaldehyde (**6**), respectively, using the procedure of Keum *et al.* [15]. The compounds were purified by column chromatography on silica gel (9:1 hexane/ethyl acetate) prior to esterification. 5-(4-Hydroxyphenyl)salicylaldehyde was prepared by formylation of 4,4′-biphenol via a Reiner–Teimann reaction. The 4′-alkoxybiphenyl-4-carboxylic acids were prepared by the procedure of Gray *et al.* [16].

2.3. *General procedure for the esterification of compounds **5** and **7***

The following procedure is representative. To a solution of **5** (51 mg, 0·17 mmol) and 4′-*n*-heptyloxybiphenyl-4-carboxylic acid (44 mg, 0·14 mmol) in 20 ml of CH_2Cl_2 were added 1,3-dicyclohexylcarbodiimide (DCC, 54 mg, 0·26 mmol) and 4-dimethylaminopyridine (DMAP, 19 mg, 0·16 mmol). The mixture was stirred at room temperature and monitored by TLC until completion of the reaction. The solvent was removed *in vacuo*, and the ester purified by column chromatography on silica gel (9:1 hexane/ethyl acetate). The ester was further purified by recrystallization from acetonitrile to give a colourless solid.

2.3.1. *1′,3′,3′-Trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl 4′-heptyloxybiphenyl-4-carboxylate (**1a**)*

Yield 70%. ^{1}H NMR δ 0·87–0·97 (m, 3H), 1·16 (s, 3H), 1·32–1·60 (m, 8H), 1·73–1·83 (m, 2H), 2·73 (s, 3H), 3·98 (t, 2H, $J = 6·5$ Hz), 5·71 (d, 1H, $J = 10·2$ Hz), 6·52 (d, 1H, $J = 7·7$ Hz), 6·70–7·21 (m, 9H), 7·56 (d, 2H, $J = 8·7$ Hz), 7·65 (d, 2H, $J = 8·4$ Hz), 8·19 (d, 2H, $J = 8·3$ Hz). MS *m/z* 587(M^+, 12), 295(44), 292(100), 213(54), 197(51), 159(95), 115(12). High-resolution MS: calculated for $C_{39}H_{41}NO_4$ 587·3036; found 587·3030.

2.3.2. *1′,3′,3′-Trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl 4′-octyloxybiphenyl-4-carboxylate (**1b**)*

Yield 91%. ^{1}H NMR δ 0·86–0·93 (m, 3H), 1·18 (s, 3H), 1·33 (s, 3H), 1·27–1·50 (m, 10H), 1·75–1·89 (m, 2H), 2·75 (s, 3H), 4·01 (t, 2H, $J = 6·5$ Hz), 5·73 (d, 1H, $J = 10·2$ Hz), 6·54 (d, 1H, $J = 7·7$ Hz), 6·72–7·18 (m, 9H), 7·59 (d, 2H, $J = 8·68$ Hz), 7·68 (d, 2H, $J = 8·4$ Hz), 8·21 (d, 2H, $J = 8·3$ Hz). ^{13}C NMR δ 165·4 159·6, 152·0, 148·1, 145·9, 143·7, 136·6, 131·9, 130·6, 128·9, 128·3, 127·6, 127·5, 126·5, 122·5, 121·5, 120·3, 119·4, 119·1, 115·6, 115·0, 106·8, 104·4,

68·2, 51·8, 31·8, 29·4, 29·2, 29·0, 26·0, 25·8, 22·9, 20·2, 14·1. UV (C_6H_{12}) λ_{max} 298 (log ε 4·49). MS *m/z* 601(M^+, 11), 309(21), 292(100), 197(12), 159(38). High-resolution MS: calculated for $C_{40}H_{43}NO_4$ 601·3192; found 601·3180.

2.3.3. *1′,3′,3′-Trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl 4′-nonyloxybiphenyl-4-carboxylate (**1c**)*

Yield 75%. ^{1}H NMR δ 0·85–0·92 (m, 3H), 1·16 (s, 3H), 1·32 (s, 3H), 1·16–1·96 (m, 12H), 2·73 (s, 3H), 3·14–3·24 (m, 2H), 3·98 (t, 2H, J = 6·5 Hz), 5·71 (d, 1H, J = 10·8 Hz), 6·53 (d, 1H, J = 7·7 Hz), 6·70–7·21 (m, 9H), 7·56 (d, 2H, J = 8·7 Hz), 7·65 (d, 2H, J = 8·4 Hz), 8·19 (d, 2H, J = 8·4 Hz). MS *m/z* 615(M^+, 9), 323(21), 292(100), 196(18), 158(83). High-resolution MS: calculated for $C_{41}H_{45}NO_4$ 615·3348; found 615·3381.

2.3.4. *1′,3′,3′-Trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl 4′-decyloxybiphenyl-4-carboxylate (**1d**)*

Yield 84%. ^{1}H NMR δ 0·85–0·90 (m, 3H), 1·16 (s, 3H), 1·32 (s, 3H), 1·30–1·96 (m, 14H), 2·73 (s, 3H), 3·12–3·24 (m, 2H), 3·98 (t, 2H, J = 6·5 Hz), 5·70 (d, 1H, J = 10·2 Hz), 6·52 (d, 1H, J = 7·7 Hz), 6·70–7·21 (m, 9H), 7·56 (d, 2H, J = 8·7 Hz), 7·65 (d, 2H, J = 8·4 Hz), 8·19 (d, 2H, J = 8·4 Hz). MS *m/z* 629(M^+, 8), 337(18), 292(100), 197(13), 159(44). High-resolution MS: calculated for $C_{42}H_{47}NO_4$ 629·3505; found 629·3523.

2.3.5. *1′,3′,3′-Trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl 4′-dodecyloxybiphenyl-4-carboxylate (**1e**)*

Yield 87%. ^{1}H NMR δ 0·85–0·91 (m, 3H), 1·18 (s, 3H), 1·33 (s, 3H), 1·27–1·55 (m, 18H), 1·78–1·86 (m, 2H), 2·75 (s, 3H), 4·01 (t, 2H, J = 6·5 Hz), 5·73 (d, 1H, J = 10·2 Hz), 6·54 (d, 1H, J = 7·6 Hz), 6·72–7·23 (m, 9H), 7·59 (d, 2H, J = 8·8 Hz), 7·68 (d, 2H, J = 8·5 Hz), 8·21 (d, 2H, J = 8·5 Hz). UV (C_6H_{12}) λ_{max} 296 (log ε 4·54). MS *m/z* 657(M^+, 7), 365(17), 292(100), 196(19), 158(71). High-resolution MS: calculated for $C_{44}H_{51}NO_4$ 657·3818; found 657·3852.

2.3.6. *1′,3′,3′-Trimethyl-6-[4-(4-pentyloxybenzoyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline] (**2a**)*

Yield 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0·95 (t, 3H), 1·18 (s, 3H), 1·33 (s, 3H), 1·31–1·47 (m, 4H), 1·83 (m, 2H), 2·76 (s, 3H), 4·04 (t, 2H), 5·74 (d, J = 10·2 Hz, 1H), 6·54 (d, J = 7·7 Hz, 1H), 6·79–7·32 (m, 7H), 6·97 (d, J = 8·8 Hz, 2H), 7·24 (d, J = 8·6 Hz, 2H), 7·56 (d, J = 8·6 Hz, 2H), 8·16 (d, J = 8·8 Hz, 2H). MS *m/z* 559(M^+, 10), 544(5), 191(22), 159(100), 144(11), 121(63). High-resolution MS: calculated for $C_{37}H_{37}NO_4$ 559·2722; found 559·2739.

2.3.7. *6-[4-(4-Heptyloxybenzoyloxy)phenyl]-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**2b**)*

Yield 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0·90 (t, 3H), 1·19 (s, 3H), 1·31 (s, 3H), 1·24–1·49 (m, 8H), 1·86 (m, 2H), 2·77 (s, 3H), 4·06 (t, 2H), 5·75 (d, J = 10·1 Hz, 1H), 6·55 (d, J = 7·7 Hz, 1H), 6·79–7·33 (m, 7H), 6·98 (d, J = 8·8 Hz, 2H), 7·25 (d, J = 8·5 Hz, 2H), 7·56 (d, J = 8·5 Hz, 2H), 8·16 (d, J = 8·8 Hz, 2H). MS *m/z* 587(M^+, 10), 572(5), 219(21), 159(100), 144(12), 121(86). High-resolution MS: calculated for $C_{39}H_{41}NO_4$ 587·3036; found 587·3061.

2.3.8. *1′,3′,3′-Trimethyl-6-[4-(4-octyloxybenzoyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline] (**2c**)*

Yield 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0·90 (t, 3H), 1·18 (s, 3H), 1·32 (s, 3H), 1·24–1·47 (m, 10H), 1·82 (m, 2H), 2·76 (s, 3H), 4·04 (t, 2H), 5·73 (d, J = 10·3 Hz, 1H), 6·54 (d, J = 7·7 Hz, 1H), 6·79–7·32 (m, 7H), 6·97 (d, J = 8·8 Hz, 2H), 7·23 (d, J = 8·6 Hz, 2H), 7·56 (d, J = 8·6 Hz, 2H), 8·15 (d, J = 8·8 Hz, 2H). MS *m/z* 601(M^+, 10), 586(5), 159(100), 144(12), 121(85). High-resolution MS: calculated for $C_{40}H_{43}NO_4$ 601·3192; found 601·3178.

2.3.9. *1′,3′,3′-Trimethyl-6-[4-(4-nonyloxybenzoyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline] (**2d**)*

Yield 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0·89 (t, 3H), 1·18 (s, 3H), 1·32 (s, 3H), 1·26–1·47 (m, 12H), 1·83 (m, 2H), 2·77 (s, 3H), 4·04 (t, 2H), 5·74 (d, J = 10·2 Hz, 1H), 6·54 (d, J = 7·7 Hz, 1H), 6·78–7·32 (m, 7H), 6·97 (d, J = 9·0 Hz, 2H), 7·23 (d, J = 8·6 Hz, 2H), 7·55 (d, J = 8·6 Hz, 2H), 8·15 (d, J = 9·0 Hz, 2H). MS *m/z* 615(M^+, 10), 600(5), 247(18), 159(100), 144(12), 121(80). High-resolution MS: calculated for $C_{41}H_{45}NO_4$ 615·3349; found 615·3338.

2.3.10. *6-[4-(4-Decyloxybenzoyloxy)phenyl]-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**2e**)*

Yield 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0·88 (t, 3H), 1·19 (s, 3H), 1·32 (s, 3H), 1·26–1·48 (m, 14H), 1·82 (m, 2H), 2·76 (s, 3H), 4·04 (t, 2H), 5·73 (d, J = 10·2 Hz, 1H), 6·55 (d, J = 7·7 Hz, 1H), 6·78–7·33 (m, 7H), 6·98 (d, J = 8·9 Hz, 2H), 7·24 (d, J = 8·6 Hz, 2H), 7·54 (d, J = 8·6 Hz, 2H), 8·15 (d, J = 8·9 Hz, 2H). MS *m/z* 629(M^+, 10), 614(6), 261(18), 159(100), 144(11), 121(90). High-resolution MS: calculated for $C_{42}H_{47}NO_4$ 629·3505; found 629·3535.

3. Results and discussion

3.1. *Synthesis*

The esters **1a–e** and **2a–e** were synthesized in 70–93% yield via DCC esterification of 6-hydroxy-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (**5**) and 6-(4-hydroxyphenyl)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (**7**) with the corresponding 4′-alkoxybiphenyl-4-carboxylic acids and 4-alkoxybenzoic acids, respectively, as shown in the scheme. The spiropyrans **5** and **7** were readily obtained by reaction of the corresponding salicylaldehydes with 2-methylene-1,3,3-trimethylindoline (**3**) [15].

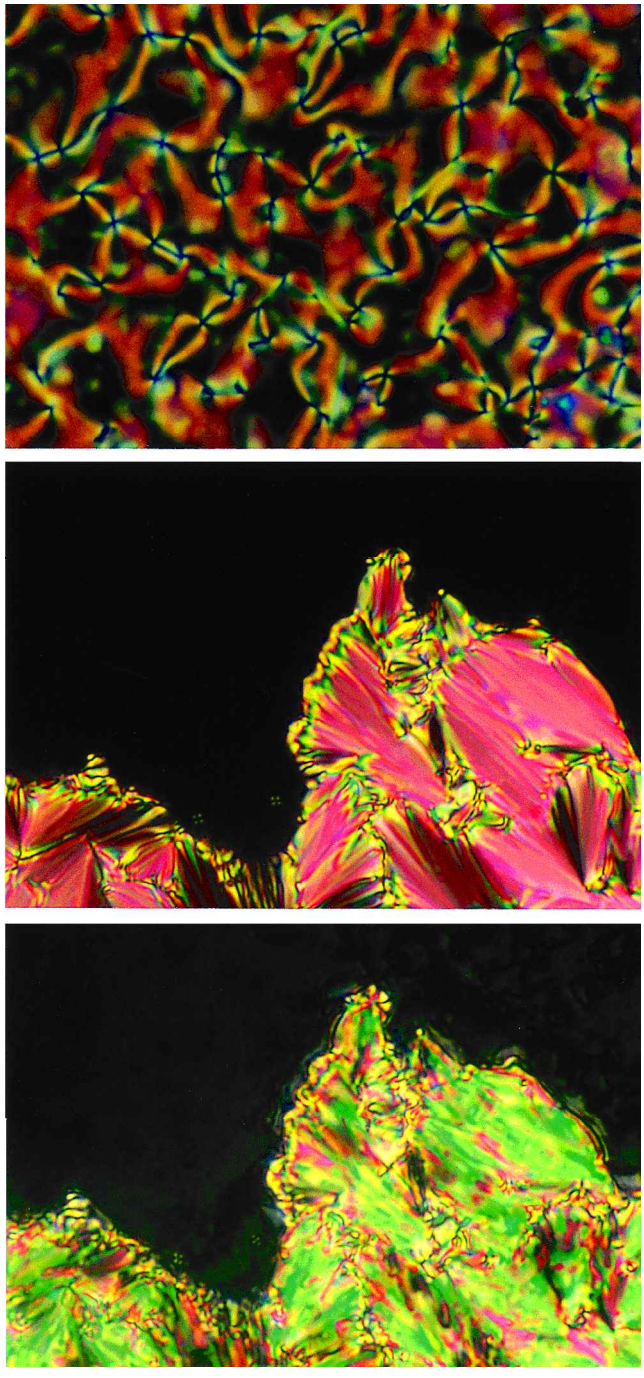


Figure 1. Textures of compound **1b** observed between crossed polarizers on cooling from isotropic liquid: 101°C, nematic phase (top); 85°C, SmA phase (middle); 68°C, SmC phase (bottom).

3.2. *Mesophase characterization*

The characterization of liquid crystal phases exhibited by the spiropyran derivatives was achieved primarily by differential scanning calorimetry and polarizing microscopy. None of the ester derivatives reported herein formed an enantiotropic mesophase. The esters **1a–d** formed nematic and SmA phases on cooling (see the table), as evidenced by the schlieren and fan textures observed by polarizing microscopy, respectively (Fig. 1). A careful examination of the DSC thermogram obtained for ester **1b** also revealed a second-order phase transition at 71°C corresponding to the appearance of a SmC phase (Fig. 2). This assignment was confirmed by polarizing microscopy, which showed the appearance of a schlieren texture in the homeotropic domain of the SmA phase along with a change of the SmA fan texture into a SmC broken fan texture (Fig. 1) [17]. The ester **1e** formed only a monotropic SmA phase. None of the esters in the series **2a–e** formed smectic phases. Analysis by DSC and polarizing microscopy indicated the formation of a

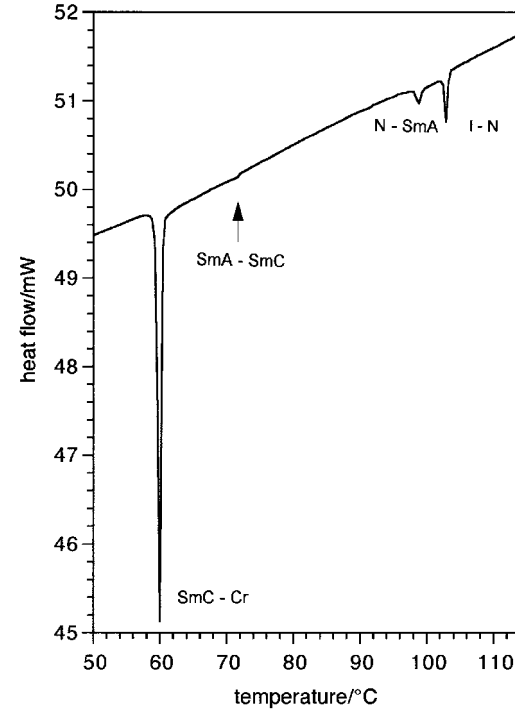
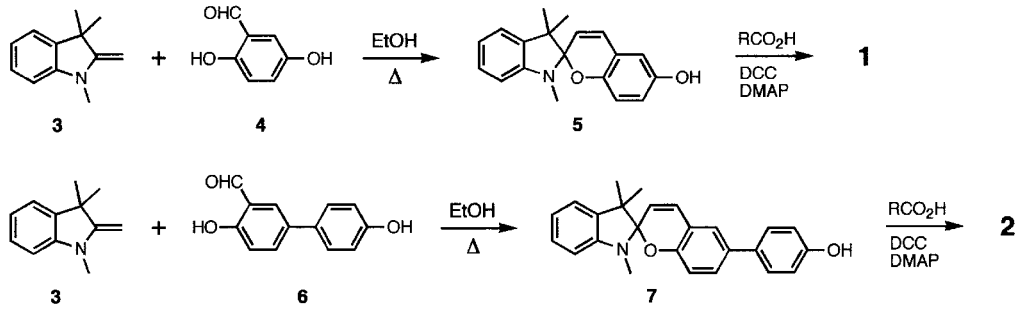


Figure 2. DSC thermogram of compound **1b** on cooling from isotropic liquid.



Scheme. Synthesis of compounds **1** and **2**.

nematic phase on cooling for compounds **2a–d** (see the table).

Analysis of compounds **1c–e** by X-ray diffraction (WAXS) at 85°C showed a wide-angle halo and a single sharp diffraction peak at small angle, which is consistent with a SmA phase. At small angle (SAXS), compound **1e** gave a single diffraction peak at a Bragg angle of 2·4°C, which corresponds to a SmA layer spacing of 37 Å. This matches the molecular length of **1e** in its most extended form (37·3 Å, MM2), and rules out the formation of dimeric aggregates. We were unable to obtain X-ray diffraction data for the SmC phase of **1c** due to its tendency to crystallize in the glass capillary tube below 70°C. Upon further cooling, all compounds exhibiting a monotropic liquid crystal phase, i.e. **1a–e** and **2a–d**, turned into amorphous solids that slowly crystallized at room temperature. Depending on the chain length, this crystallization period ranged from a few hours to several days.

4. Conclusions

Two series of novel mesogens incorporating a non-activated spiropyran moiety have been synthesized. Among the compounds investigated, the 4′-octyloxybiphenyl-4-carboxylate derivative **1b** was found to exhibit a monotropic SmC phase. To the best of our knowledge, it is the first example of a spiropyran-containing SmC mesogen to be reported. However, due to the propensity of aromatic esters to undergo photo-Fries rearrangements, these compounds are unsuitable for optoelectronics applications. Nevertheless, this work has shown that it is possible to incorporate a non-activated spiropyran into a SmC mesogen, and further work aimed at developing photostable spiropyran-containing SmC mesogens is in progress.

Table. Transition temperatures of 1′,3′,3′-trimethylspiro-[2*H*-1-benzopyran-2,2′-indoline]-6-yl 4′-alkyloxybiphenyl-4-carboxylates (**1a–e**) and 6-[4-(4-alkoxybenzoyloxy)phenyl]-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indolines] (**2a–e**) on cooling from isotropic liquid.

Compound	Cr		SmC		SmA		N		I
1a	•	78	—		•	104	•	107	•
1b	•	60	•	71	•	99	•	103	•
1c	•	72	—		•	90	•	94	•
1d	•	77	—		•	93	•	96	•
1e	•	72	—		•		—	92	•
2a	•	72	—		—		•	102	•
2b	•	69	—		—		•	97	•
2c	•	76	—		—		•	91	•
2d	•	65	—		—		•	89	•
2e	•		—		—		—	93	•

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